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Molecular motion in polymer thin films exhibits fast and slow subpopulations. KEEWOOK PAENG, MARK EDIGER, University of Wisconsin-Madison — The reorientation of dilute fluorescent probes in thin polymer films was studied using a photobleaching technique. The existence of two subsets of probe molecules with different dynamics was revealed by temperature-ramping and isothermal anisotropy measurements. For freestanding polystyrene films, the slow subset shows bulk-like dynamics while the more mobile subset reorients 4 orders of magnitude faster at Tg - 5 K. The difference in dynamics becomes larger as temperature decreases and disappears as temperature approaches Tg. We interpret the fraction of the sample with fast dynamics as a high mobility layer at the film surfaces. The thickness of this mobile surface layer increases with temperature and does not depend on the molecular weight of the polymer and total film thickness. The mobile surface layer exists in various freestanding polymer thin films including polystyrene and poly(methyl methacrylate) and is also present in supported films of these polymers.

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